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Slow Dynamics and Aging of a Colloidal Hard Sphere Glass

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The intermediate scattering function (ISF) is measured for a colloidal hard-sphere glass as functions of the scattering vector and waiting time. For scattering vectors near the structure factor peak, we show that the ISF and the stretching index, defined at the crossover time between the fast and slow processes, depend algebraically on the waiting time. By contrast, the Debye-Waller factor is independent of the waiting time.

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Upon quenching, by either increasing the density or decreasing the temperature, a fluid experiences a first order transition to a crystalline solid. Alternatively, depending on the quench depth and the fluids' complexity, it forms an amorphous solid. The latter, unlike the thermodynamically equilibrated crystal, exhibits aging—slow, nonstationary dynamics [1], effected through rare, intermittent structural rearrangements [2]. It is evident from work over about the last decade, that amorphous soft matter lends itself particularly well to the study of aging. Foams, colloidal gels and glasses, and clays such as laponite, all exhibit aging behavior (for reviews see [3,4]). In these mesoscopic materials the dynamics are generally accessible by optical techniques, expressed for instance, by the dependence of the intermediate scattering function (ISF), or an intensity correlation function, on delay time and waiting time.

Despite their diversity, the ISFs of these soft solids are generally found to decay in two stages: an initial decay onto a plateau, followed by a final age dependent decay. The plateau height, a feature indicative of the materials elasticity, is in many cases observed to be nonstationary [2,5]. The aging characteristics of these materials are also complex and sample dependent [3]. For laponite glasses, for example, some workers have identified two aging regimes: an initial process, where the aging is an exponential function of waiting time, and a ''full'' aging regime, where the aging is a linear function of waiting time [6]. Recent work has suggested that the exponential regime is related to the liquid-glass transition upon cessation of shear, rather than true aging of the glass [7]. By contrast, other workers have found power law aging with exponents of order ~ 1.8 [8]. Clearly aspects of aging in these systems are still to be fully understood.

In this Letter we turn to a suspension of particles whose interactions are like those of hard spheres. This system exhibits both a first order (freezing-melting) transition and a glass transition [9,10], and while it presents a simpler soft amorphous solid than those described above, its aging behavior is the subject of only a few studies to date. Amongst these are confocal microscopy studies showing that the mean square displacement exhibits significant aging, but the aging showed only weak correlation with structural changes [11]. Since the first observation of aging behavior in a hard-sphere glass [1], to our knowledge the only light scattering study is that of El Masri *et al.* [12], who observed aging in measurements of the intensity correlation function. The relaxation times measured for high volume fractions show aging at early times, with a possible plateau at later waiting times.

The particles used in the experiments reported here comprise cores of methylmethacrylate (MMA) and trifluoroethyl acrylate (TFEA) and coatings, approximately 10 nm thick, of poly(12-hydroxystearic acid). Their average hydrodynamic radius ($R = 200$ nm) and polydispersity (6%), were determined by DLS on very dilute samples. Suspension of the particles in cis-decalin achieves optical matching to a degree that effectively suppresses multiple scattering over the range of wave vectors, $1.5 < qR < 4.15$, spanned in these experiments. The lack of detectable charge on the particles, means that the interactions between them are dominated by a short range repulsion effected by the solvated surface coating [13]. Hence these suspensions present a good approximation to the perfect hard-sphere system. Accordingly, after mapping the suspension's equilibrium phase behavior onto that known for the perfect hard-sphere system, the volume fractions $\phi_f = 0.493$ and $\phi_m = 0.545$ of coexisting fluid and crystal phases can be identified [9]. In addition these suspensions exhibit a glass transition at $\phi_g \sim 0.57$ [10,14]. Preparation of samples is described in detail in [15,16].

In a glass the movements of the particles are restricted to such an extent that they are unable to randomize the phase of the (coherent) light in an experiment of reasonable duration. In other words the time average is no longer equal to the ensemble average—i.e., the sample is nonergodic. To make statistically valid measurements on such systems, nonergodic averaging techniques must be employed [1,17,18]. Expediency dictates that separate procedures be adopted to capture the fast processes and the slow, aging processes. Accordingly, the initial decay of the ISF, $f(q, \tau)$, is determined by the procedure developed by Pusey and van Megen [17,18] for dynamic light scattering by nonergodic media. In this it is assumed that density fluctuations can be decomposed into an arrested, time invari-

ant, component, and a fluctuating component associated with local motions about fixed average positions. The resulting scattered light field comprises constant and fluctuating components. Then, provided the spatial correlation of both components is much smaller than the linear dimension of the scattering volume, the fluctuating field is a complex, Gaussian variable of zero mean. These considerations lead to the following expression for the ISF [18];

$$f(q,\tau) = 1 + \frac{\langle I\rangle_T}{\langle I\rangle_E}\left\{\left[\frac{\langle I(0)I(\tau)\rangle_T - \langle I^2\rangle_T}{\langle I\rangle_T^2} + 1\right]^{1/2} - 1\right\}, \tag{1}$$

where τ is the delay time, $\langle\ldots\rangle_T$ refers to the time average over the intensity fluctuations of a single speckle (or spatial Fourier component of the particle number density fluctuations) accumulated in a single measurement of duration T, and $\langle\ldots\rangle_E$ refers to the ensemble average, acquired by averaging over a large number ($\approx$4000) of speckles, achieved here in a single rotation of the sample. The nonergodicity parameter, or Debye-Waller factor, $f(q,\infty)$ follows from Eq. (1) in the limit $\tau \to \infty$:

$$f(q,\infty) = 1 + \frac{\langle I\rangle_T}{\langle I\rangle_E}\left\{\left[2 - \frac{\langle I^2\rangle_T}{\langle I\rangle_T^2}\right]^{1/2} - 1\right\}. \tag{2}$$

Previous work confirms the validity of this method, at least for the hard-sphere colloidal glass [19]. In that the derivation of the above assumes that the ISF decays through Gaussian density fluctuations to a constant, finite value, $f(q,\infty)$, the dynamics are presumed stationary during the course of a measurement of duration T. In turn, this places an upper limit on the dynamic window where stationarity is (at least approximately) maintained. For the colloidal glass studied here we find, by conducting measurements with a range of accumulation times T, that stationarity is observed for delay times up to approximately 10 s. So the ISF, $f(q, 10^{-6} < \tau \leq 10$ s), obtained by analyzing, according to Eq. (1) and (2), the intensity fluctuations of a single speckle, shows no systematic variation with waiting time. As in previous work [20], the "brute force" technique was used to confirm the results.

Slower decays are measured with the method of echoes introduced by Pham *et al.* [21]. In this method a slow, continuous rotation of the sample effectively provides an average over some ($\approx$4000) speckles from which the ensemble average of the time autocorrelation function of the intensity of the scattered light is constructed. The results of the two methods are combined in the manner described in [1]. As a check, the interleaved sampling technique [1,22] was used in parallel, and the results are consistent with the echo results reported here. Also, by varying the rotation rate and the duration of the rotation, it was established that the results are not affected by rotation of the sample for rotation rates of order 1 s^{-1}. Prior to the start of a measurement the sample was tumbled for at least 24 hours and the waiting time origin, $t_w = 0$, is defined as the time tumbling stopped. All times are expressed in terms of the Brownian time $\tau_B = \frac{R^2}{6D_0} = 0.0207$ s, where D_0 is the free diffusion coefficient.

Figure 1(a) shows typical ISFs at $\phi = 0.58$ for several waiting times at a qR value near the primary maximum in the static structure factor. In all cases a shoulder, or plateau, separates a fast process, with no apparent dependence on the waiting time, and a slow process that stretches out as t_w increases. One sees that the ISF's do not decay to zero even in the time window which, in this case, spans almost nine decades. This contrasts with the results of more complex soft solids, where the measured correlation functions decay fully, or almost fully, in the accessible time window [2,3,6,8,23]. The inset on the left shows the ISF for several values of qR at a waiting time of 10 h ($\frac{t_w}{\tau_B} \simeq 1.7 \times 10^6$).

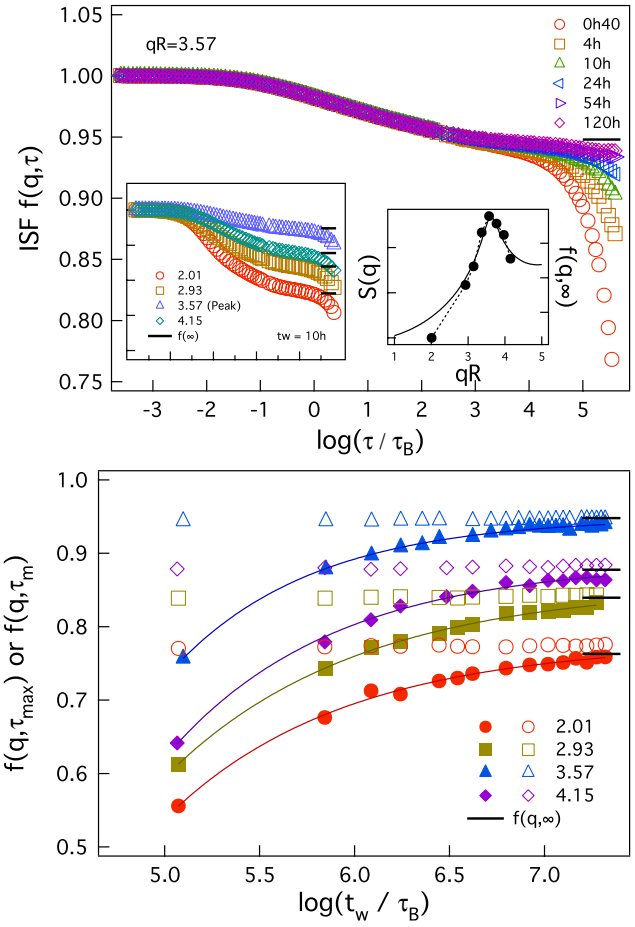

FIG. 1 (color online). (a) The ISF for the waiting times indicated, at the structure factor peak ($qR = 3.57$). The left inset shows the ISF for a sample age of 10 h at several values of qR around the structure factor peak. The right inset shows the Percus Yevick structure factor for hard spheres along with the nonergodicity parameter from Eq. (2). These values are also shown as the black lines in the left inset and the main graph. (b) $f(q,\tau_{\max};t_w)$ (closed symbols) and $f(q,\tau_m)$ (open symbols) as functions of the waiting time for several values of qR. $\tau_{\max} \sim 4 \times 10^5$ is the upper limit of the time window. Lines are power law fits to the data. The nonergodicity parameters, $f(q,\infty)$, obtained from Eq. (2), are shown as horizontal lines.

The measured values of $f(q, \infty)$, obtained by Eq. (2), are plotted in the second inset of Fig. 1(a). As found in [19], $f(q, \infty)$ varies in harmony with the static structure factor. Despite the limited decay of the ISF, mentioned above, the aging process can still be quantified by plotting, in Fig. 1(b), the ISF at the upper limit of the time window, $f(q, \tau_{\max}; t_w)$, as a function of t_w. The lines are power law fits of the form: $f(q, \tau_{\max}; t_w) = A(q)[1 - (\frac{t_w}{t_o})^{-b}]$. At the structure factor peak, $b = 0.59$ and $t_o = 8300$. The values of these parameters vary by less than 20% over the q range studied. The values of $A(q)$, shown as horizontal lines in Fig. 1(b), agree with $f(q, \infty)$, to within 1%. Our analysis for other delay times gives the same values for $A(q)$. It is already apparent from Fig. 1(a) that the waiting time dependence of $f(q, \tau)$ decreases as τ decreases; it is most pronounced at $\tau = \tau_{\max}$, but almost imperceptible at the crossover, τ_m (defined below), from the fast process to the slow aging process.

This crossover can be quantified by analysis of the "width" function, defined by analogy with the mean-squared displacement, as

$$w(q, \tau) = -q^2 \ln f(q, \tau). \tag{3}$$

This function is shown in Fig. 2(a). If the relaxation of the particle number density fluctuations were diffusive, $w(q, \tau)$ would increase in proportion to τ, and its logarithmic slope,

$$n(q, \tau) = \frac{d \log(w(q, \tau))}{d \log \tau} \tag{4}$$

would be one, for all τ. Obviously, this is far from the case. It is evident from the inset in Fig. 2(a) that $n(q, \tau)$ has a minimum, $\nu(q) = \min[n(q, \tau)]$ at τ_m, that deepens with age. As in [24–26] we identify τ_m as the crossover time between the fast process, $f(q, \tau < \tau_m; t_w)$, and the slow process, $f(q, \tau > \tau_m; t_w)$, and the stretching index, $\nu(q)$, as a measure of the coupling between them. Figure 2(b) shows that the waiting time dependence of $\nu(q)$ can be described by a power law; $\nu(q; t_w) = (\frac{t_w}{t_x})^{-\varsigma}$. The value, $\varsigma = 0.19 \pm 0.02$, of the exponent shows no systematic variation with q, but t_x scales approximately with $S(q)$ [as shown in the inset to Fig. 2(b)].

From the ISF we calculate the autocorrelation function of the longitudinal current [27]

$$C(q, \tau) = -\frac{d^2}{d\tau^2} f(q, \tau). \tag{5}$$

This quantity is found to decay to zero from below, and is best exposed by plotting its absolute value, as shown in Fig. 3. Note that the smoothing of the data demanded by numerical differentiation has reduced the maximum delay time of $|C(q, \tau)|$ to $\tau'_{\max} = 8 \times 10^5 (= 1500$ s). The simplest function that describes the last decades of the decay is a power law; $|C(q, \tau)| = (\frac{\tau}{\tau_c})^{-\sigma}$: the exponent $\sigma = 2.15 \pm 0.1$ shows little q dependence, but the scaling time τ_c varies inversely with the structure factor and has a minimum value of ~5 at q_m.

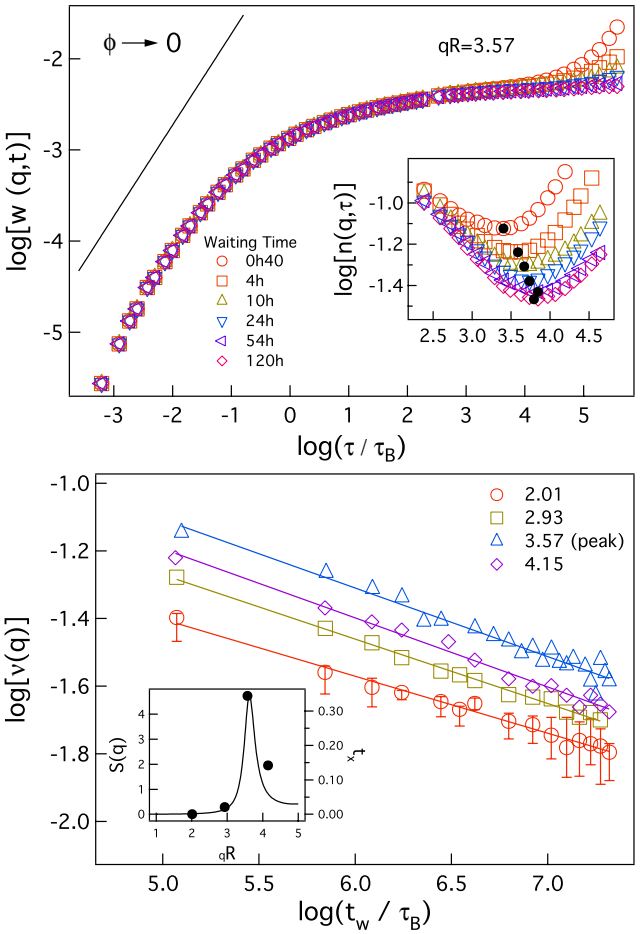

FIG. 2 (color online). (a) The width function [Eq. (3)] as a function of delay time at $qR = 3.57$ for the waiting times indicated. Inset: $n(q, \tau)$ [Eq. (4)] in the echo DLS range, where the inflection is observed. The minima are indicated by the filled symbols. (b) The stretching index as a function of the waiting time for several scattering vectors. Inset shows the Percus Yevick structure factor. The prefactors of the power law fit are also represented in this inset. Except where indicated the error bars are smaller than the symbols.

The observation of a negative algebraic decay with a negative exponent of (approximately) two is not without precedent. It has also been found in the velocity autocorrelation function—the correlation function of the single particle current—measured on approaching the glass transition from the fluid side in hard-sphere colloidal suspensions [26,28]. In that work it was argued that negative algebraic decays are incompatible with diffusing momentum current.

It is evident that the longitudinal current correlator exhibits very little aging—most of the dependence on waiting time shown by the ISF is absent from its second derivative.

The results presented here are for one volume fraction. Measurements at other volume fractions and other latex

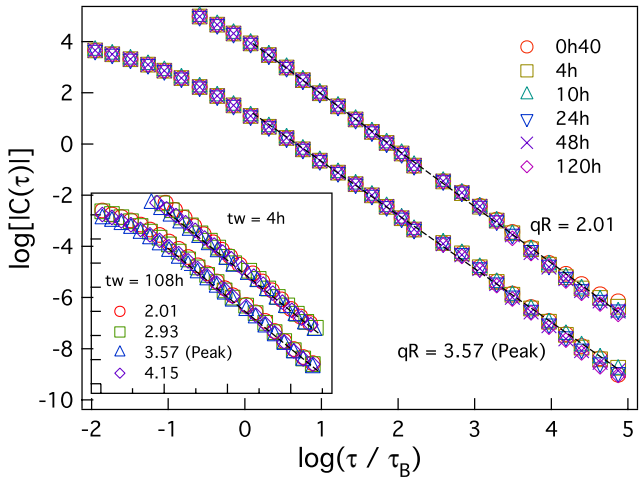

FIG. 3 (color online). The current correlator [Eq. (5)] as a function of delay time at two q vectors and a range of waiting times. The $qR = 2.01$ data have been offset for clarity. Inset: four q vectors at two different waiting times (offset for clarity). Best fitting straight lines are shown.

samples show similar trends, and will be presented elsewhere. The key result of this study is that following the quench the ideal "aged" glass, defined by $f(q, \tau \rightarrow \infty) = A(q)$ and $\nu(q) = 0$, the state in which particles perform limited motions about fixed average positions, is approached algebraically with age, but the Debye-Waller factor is independent of age.

We close with a conjecture about aging in terms of the mechanisms by which thermal energy is dissipated. For a system in thermodynamic equilibrium, hydrodynamics dictates that a particle loses its thermal energy via propagating and diffusing momentum currents—sound and flow, respectively. However, in a glass, to the extent that flow is suppressed, the thermal energy is forced into propagating modes which, in deference to the amorphous nature of the glass, are further constrained to be longitudinal. The latter stabilizes the force chains of particles, as pictured, for example, in [29]. So if a stress, in this case any unrelieved (local) thermal stress, has a direction other than that of the force chain, the material may restructure through collapse of these force chains. In this sense the glass, unlike the crystalline solid, is fragile. That the Debye-Waller factor, $f(q, \infty)$, is unaffected, at least for those spatial frequencies in the vicinity of the structure factor peak, suggests that the structural changes—fracture or local slip—may have a length scale far greater than the distance between neighboring particles. The aging of the Debye-Waller factor observed in Laponite at small q is not inconsistent with these conjectures [5].

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